A NOTE ON BINARY ALLOYS

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ABSTRACT. The binary alloys of some metals like Cu, Ag and Au can be expressed by approximately definite chemical formula and are known as abnormal valency inter metallic compounds. The different phases of these alloy systems have definite electron-atom ratios which are generally expressed as 1 4, 3/2, 21/13 and 7/4 for α, β, γ and ϵ phases respectively. They can, however, be expressed more uniformly as 21/15, 21/14 21/13 and 21/12. This regularity suggests the possibility of this being extended inside the α-phase also. The α-phase may, then, be composed of several minor phases of electron-atom ratios, 21/16, 21/17, 21/18, 21/19, 21/20, at the boundaries of which there will be discontinuities, however, small, of some physical properties of the alloys. The indications of such discontinuities found in the published data are discussed.

BINARY ALLOYS

It is found from a study of the phase diagrams of the various binary alloy systems, that the intermediate phases do not at once begin to form as soon as small amounts of one metal is added to the other. The parent metal has a capacity to absorb in its own matrix a certain amount of the 2nd metal. The lattice unit will, of course, be distorted but the distortion does not proceed indefinitely ; a stage is soon reached when a new phase with different lattice structure begins to appear. The two alloys existing at the two ends of the phase diagrams and in which the characteristics of the original lattice structures are retained, are called the primary solutions. The extent of these primary solid solutions in the case of the substitutional alloys, in which the atoms of the second metal replace those of the original, will, naturally, depend upon the relative sizes of the two kinds of atoms. From a large number of observations Hume-Rothery concludes that when the atomic diameters are within 14% of each other an extended solid solutions can be expected. It is not, however, always effective ; for instance, the amount of Zn retained in the copper-matrix is much greater than that of Cu in the Zn-matrix though they have mutually favourable size-factors. This type of solid solutions indicate that besides size-factors, the valencies of the solvents and solutes play an important part in determining the amount of a metal which can be taken into solution by other metals. If we examine the intermediate phases, *e. g.*, the binary alloys of Cu, Ag or Au, which are known as the abnormal valence intermetallic compounds (as opposed to the normal valence intermetallic compounds like Mg_3Sb_2, Mg_3Bi_2, Zn_3Sb_2, MgSe, CaTe, etc.) it will be found that the size-factor alone is insufficient to explain the observed solubilities. The β-phases of the Cu-Zn, Cu-Al and Cu-Sn alloy systems are of the compositions Cu-Zn, Cu_3Al and Cu_5Sn ; thus with the increasing valencies the amounts of the second metals become smaller though they have more or less favourable size factors. It, therefore, becomes quite evident as has, first, been pointed out by Hume-Rothery that the valencies have to be taken into

consideration to understand the extent of mutual solubilities of metals. The one important fact which comes out of the above observations is the following :—The valencies of Cu, Zn, Al and Sn being respectively 1, 2, 3 and 4, the electron-atom ratios of these abnormal valence compounds become identical namely 1. 5. A large number of the β-phase abnormal valency intermetallic compounds have been found to yield the same ratio. Further investigations have shown that the other phases of the above type of alloy-systems also have different but constant electron-atom ratios. The γ-phases of Cu-Zn, Cu-Al and Cu-Sn systems have approximately the compositions Cu_5Zn_8, Cu_9Al_4 and $Cu_{31}Sn_8$; with the valencies mentioned above the electron-atom ratio in each case becomes 21:13. The ϵ-phase of the above systems having approximate compositions $CuZn_3$, Cu_3Sn and Cu_5Al_3 yield an electron-atom ratio 7:4. The end of the α-phase solid solution has 1.4 as its electron-atom ratio. These electron-atom ratios are only approximate, the compositions of these phases being variable within certain limits. These approximate ratios of the abnormal valency intermetallic compounds which are the subject matters of the present note, have been empirically obtained by different workers, including Hume-Rothery, from a large number of observations on various alloy-systems. All phases of each and every alloy system have not been studied or do not yield the exact ratios on account of unfavourable size factors or some other reasons. The ratios obtained from observations agree well with those obtained by theoretical calculations based on quantum mechanics. The average electron-atom ratio of the α-phases of a large number of alloy systems is found to be 1.39 and its theoretical value is 1.36. The corresponding values for the β and γ phases are 1.49 and 2.48 ; 1.59 and 1.54 respectively. These values have been obtained on the assumption that the following are the valency-electrons of the respective metals.

Metals	...	Cu	Ag	Au	Zn	Cd	Hg	Al	In	Ga	Sn	Si	Se	Ni
Valencies	...	1	1	1	2	2	2	3	3	3	4	4	4	0

The electron-atom ratios, it should be noted, determine the crystal structures and the accepted values for the α, β, γ and ϵ phases are 1.4, 1.5, 21/13 and 7/4 respectively. For the γ-phase besides the ratio, 21/13, the number 13, has been found to be of considerable significance. The γ-brass for instance, has the body-centered cubic structure ; for this structure there are two atoms per unit lattice. If the parameter is given three times its value for the actual unit crystal there will be 27 units in the enlarged lattice and the expected number of atoms in it will be 54. But there has been found a distortion in the lattice, the actual number of atoms being 52 or 4×13.

The random values of these ratios can be expressed more uniformly in the following way, retaining the ratio for the γ-phase as it is—21/15, 21/14, 21/13 and 21/12 for the α, β, γ and ϵ phase respectively. The ratios have now taken very interesting forms ; they are perhaps of more significance in view of the observation regarding the γ-phase. For the same constant numerator the denominator changes by unity from one phase to the next,

i.e., a change of one atom per 21 electrons brings about a change of phase—a change of crystal structure and of many other physical properties. If one starts adding, for instance, Zn to pure Cu, the Cu-lattice retains its own structure till the electron-atom ratio increases (from 1 : 1) to 21 : 15. A rather unstable equilibrium is then reached when for every change of one atom a new phase is developed up to the ratio, 21 : 12. The next and the last ratio, 21 : 11 is not very much different from that for pure zinc namely 21 : 10.5 or 2 : 1. Pronounced phase characteristics very much different from those of Zn will then be absent. A different phase δ or η after ϵ phase is some time found in some alloy systems but it lacks regularities of the characteristics shown by the earlier phases. It should, of course, be remembered that to decrease the total number of atoms by one, one has to add one Zn-atom for two Cu-atoms removed so as to leave the number of electrons the same.

Turning to the Cu-rich side of the primary solid solution we find the margin very wide ; we can remove 6 Zn-atoms one at a time and add in their places 12 Cu-atoms in 6 equal steps till the electron atom ratio reaches its pure copper value, namely, 1 : 1. Though the phase characteristics will be determined mostly by copper it is not altogether improbable that some minor phase characteristics may in this range be evident if the regularities in the electron-atom ratios shown above are not merely accidental. The possible electron-atom ratios inside the α-primary solid solutions are 21/16, 21/17, 21/18, 21/19 and 21/20 the corresponding atomic percentage of Zn being 31, 23, 16.5, 10.5 and 5. This is true only when the second metal is divalent. For higher valencies the percentages will be proportionately smaller ; for trivalent metals they will be halves of the above, for quadrivalent, thirds. The last few will not, of course, differ widely from the pure copper ; but one or two near the end of the α-phase may produce minor discontinuities in some properties of the α-alloys. The crystal structure of the Cu Zn α-alloy which has been investigated by Owen and Pickup (1933) does not show any marked discontinuities in the gradual increase in its parameter ; the points do not either line in a smooth curve. Only a few points in the full range have been examined and accidentally most of these points are situated mostly in the regions of the expected breaks. More systematic work will be necessary to locate the discontinuity, if any, in the lattice dimension. Fairbank (1944) carried out in an exhaustive manner the measurements of the electric resistivities of the Cu-Zn and the Cu-Sn alloys at different temperatures. In the curve for Cu-Zn at 29.3° abs. it will be noticed that the resistivity for the annealed specimen rises to a maximum (conductivity reaching a minimum) near 30 atomic % of Zn. This is exactly the composition giving an electron-atom ratio of 21/16, the next lower one to that for the α-phase. Smith (1930) worked on the same problem previously and carried out measurements of both electrical and thermal conductivities of the Cu Zn and other alloys. The curve given by him for the conductivity of the Cu-Zn alloys at 20°C (293° abs.) shows a minimum (or maximum for resistivity) at about 40 atomic

percent of Zn—the end of the α-solid solution. Fairbank obtained the alloys from Smith who had these made by the American Brass Company. It can be assumed that the materials used in both these investigations were of the same consistency. In the case of the Cu-Zn alloy system, therefore, a distinct phase does make its appearance at 14.3° abs. The Cu-Sn curve for the annealed specimen at 20.4° abs, has also started drooping before 6 atomic percent of Sn has been added to Cu. It is quite likely that there will also be a maximum long before 13 atomic percent of Sn is added to Cu—this being the expected end of the primary solid solution of the Cu-Sn alloys system. The end of the primary of solid solution of Cu-Sn determined by the X-rays investigation also corresponds to an electron-atom ratio, 1 28 only instead of 1.40, the accepted value for the α-phase. This value is too low to be explained by experimental inaccuracies ; it is, however, approximately equal to 21/16 the next lower one to 21/15 or 1.40. The Cu-Zn alloy system gives an electron-atom ratio of 1.22 for its α-phase which is equal to 21/17 two steps lower to 21/15. The lower values for the Cu-Sn and the Cu-In α-phases have been attributed by Hume-Rothery to their unfavourable size-factors. Even with the unfavourable size factors the electron-atom ratios are found to belong to the series. For the α-phase of the Cu Sb alloy it is found to be 1.23 which is again equal to 21/17 instead of 21/15, the usual value for the α-phase. The solubility of Cd is extremely low,—only 1.7 atomic per cent of Cd dissolving in Cu. This gives an electron-atom ratio of 1.02 which is not far from 21/20 (1.05), the last member of the series. From the above discussion it thus appears that the electron-atom ratios for these groups of binary alloy systems, belong to a series, 21/20, 21/19...21/12 ; the first 5 members fall within the α-phase the accepted values for the latter being 21/15. The lower values of the electron concentration for the α-phase of the different alloy systems are approximately equal to one or the other of the above ratios. The electrical conductivity of the Cu-Zn systems at 14°C corresponds to the concentration 21/16 but at 293° abs. it gives the usual value of 21/15.

These minor phases inside the α-phase may be of the nature of the superlattice formation. The electron atom ratios referred to above and those of the main phases perhaps are responsible for super-lattices. It is, however, suggested that the physical properties of these types of alloys should be more critically studied (within the range of the α-solid solutions) to see if there are any small discontinuities.

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